Nanomaterials

Lecture 10: Scanning Probe Lithography

Atomic Force Microscopy Nanofabrication

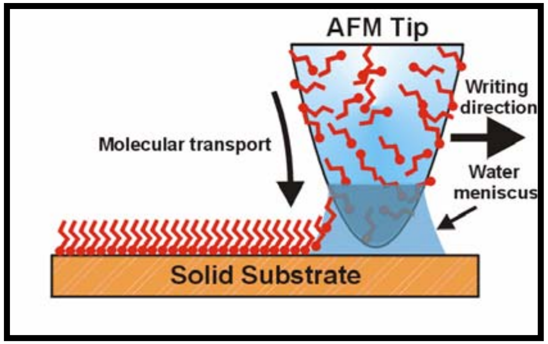
Many nanofabrication schemes have been developed with AFM (generally, spatial resolution is approximately 10 nm):

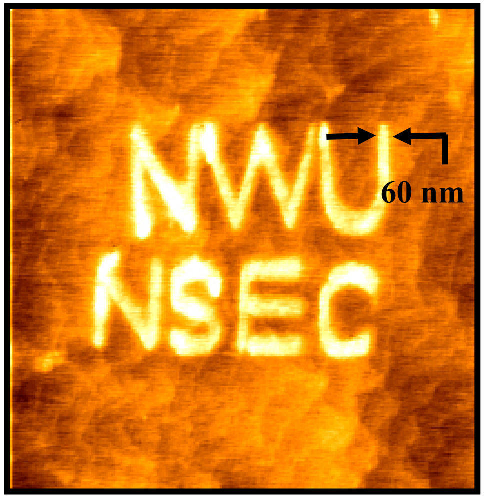
(1) Dip-pen nanolithography

(2) Scratching, pushing

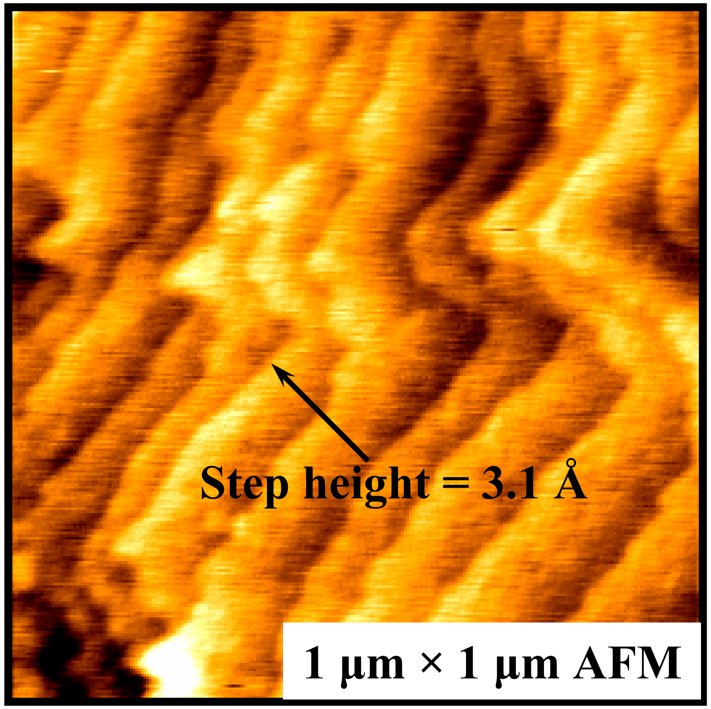
(3) Electrochemistry

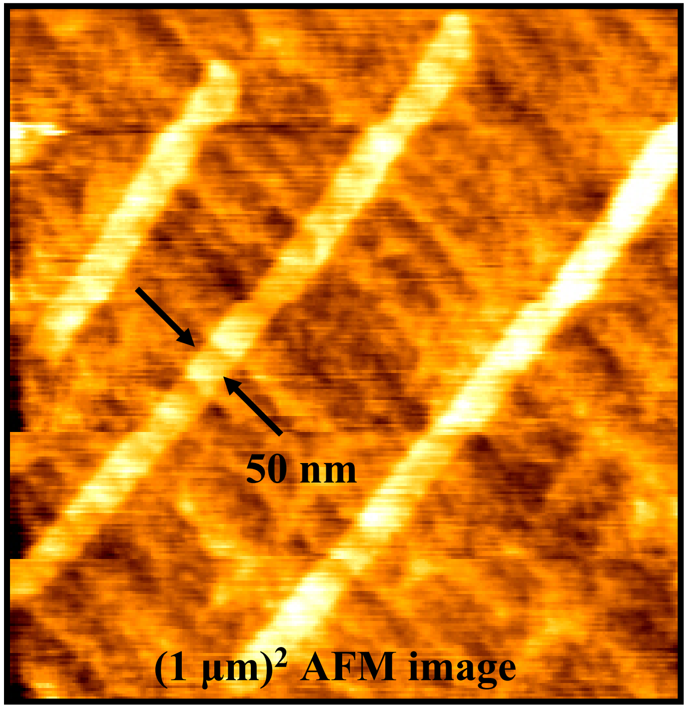
(4) Tip-induced oxidation





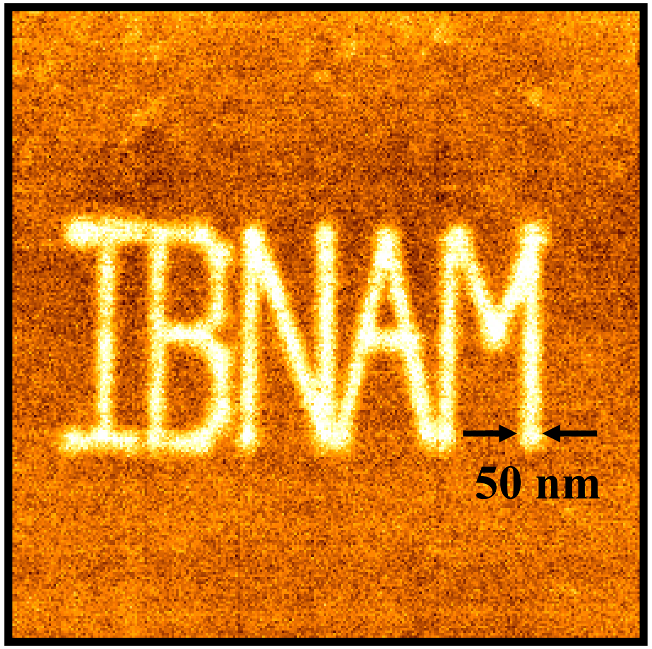
Nano Oxidation of Silicon with Conductive AFM

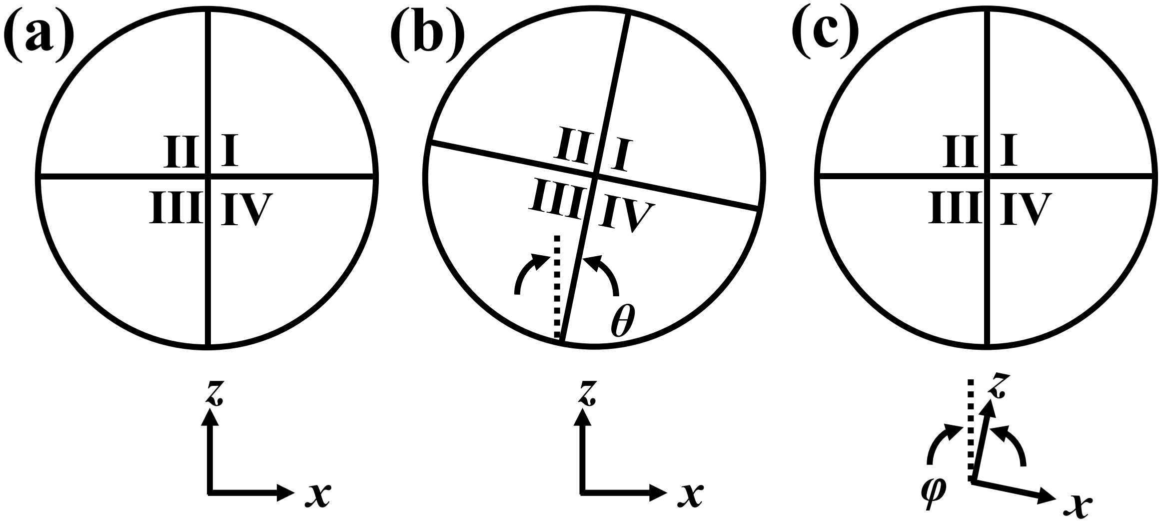




- Oxide nanopatterns achieved via local anodization of Si(111):H
- Spatial resolution limited to ~10 nm.

Lateral Force Microscopy



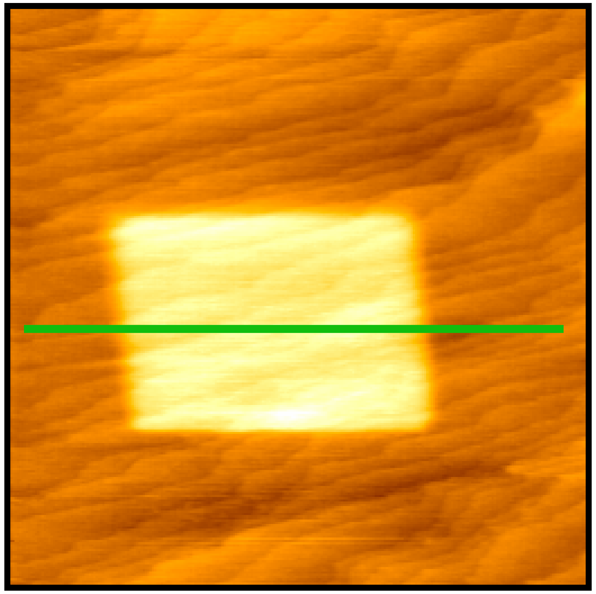


- Chemical contrast monitored via frictional force.
- Care must be taken to extract quantitative LFM data.

M. W. Such, D. E. Kramer & M. C. Hersam, *Ultramicroscopy*, 99, 189 (2004).

Selective Polymerization Chemistry

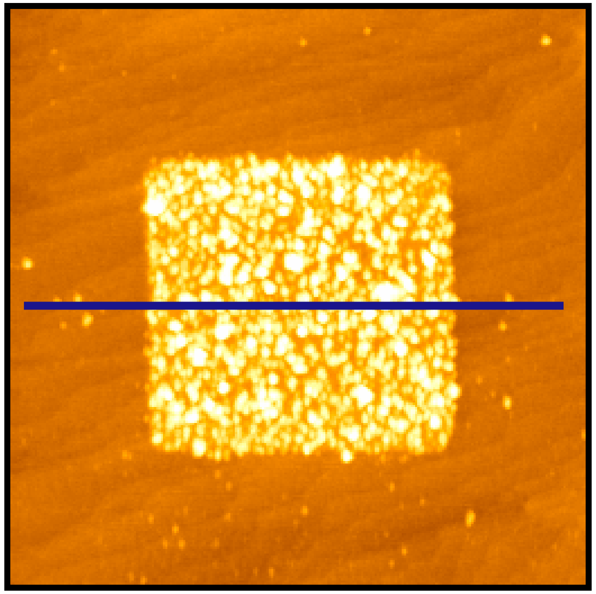
Before ROMP: 1 µm FIO



2 µm x 2 µm

7 V Sample Bias

After ROMP: 1 µm FIO



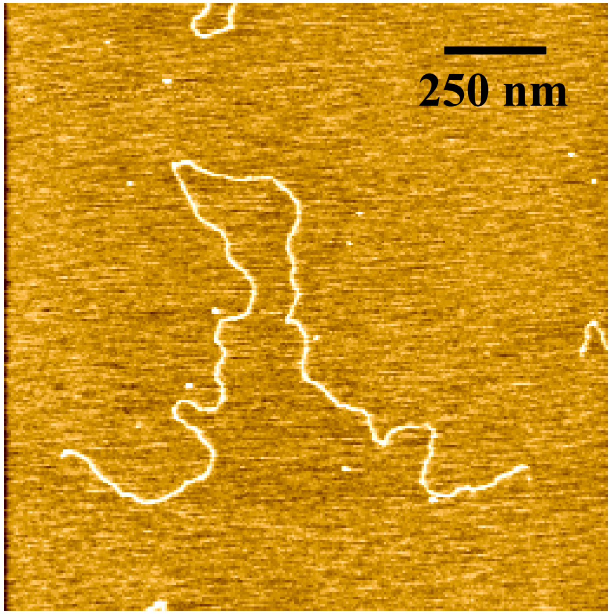
2 µm x 2 µm

ROMP = Ring Opening Metathesis Polymerization

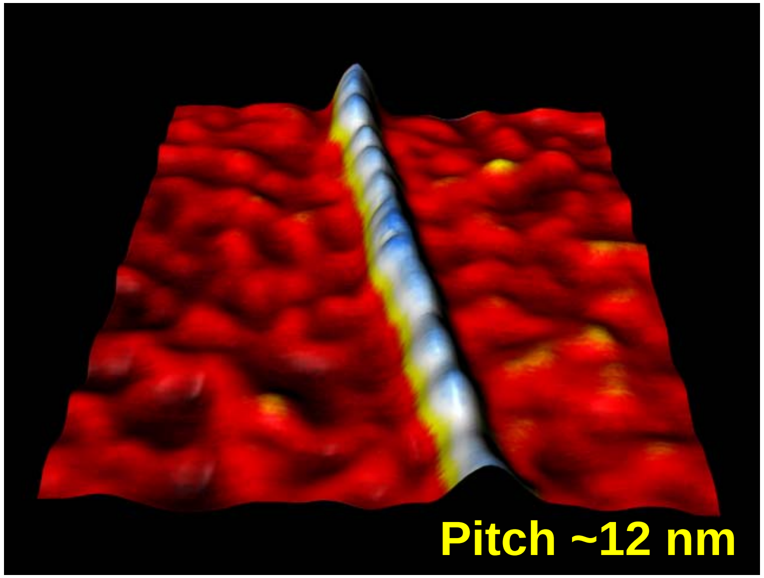
Collaboration with SonBinh Nguyen

"Single Molecule Imaging" with Ambient AFM

DNA Molecules

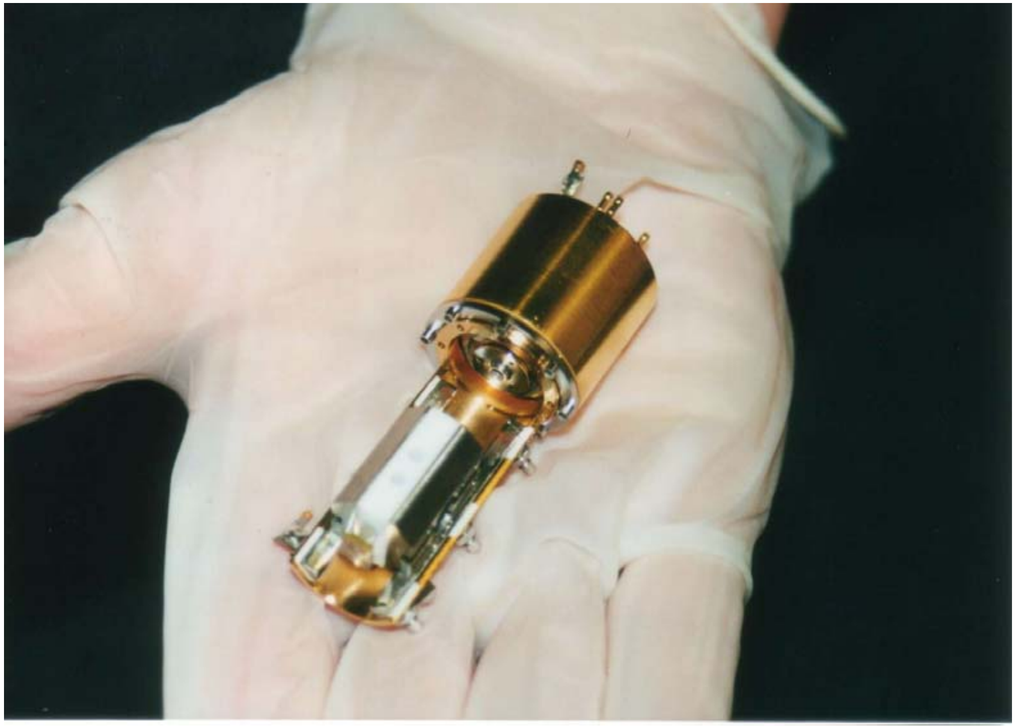


DNA Wrapped SWNTs



Typical ambient AFM resolution is ~10 nm as opposed to atomic resolution for STM → STM is typically the technique of choice for intramolecular spatial resolution imaging

Example Ultra-high Vacuum (UHV) STM Design



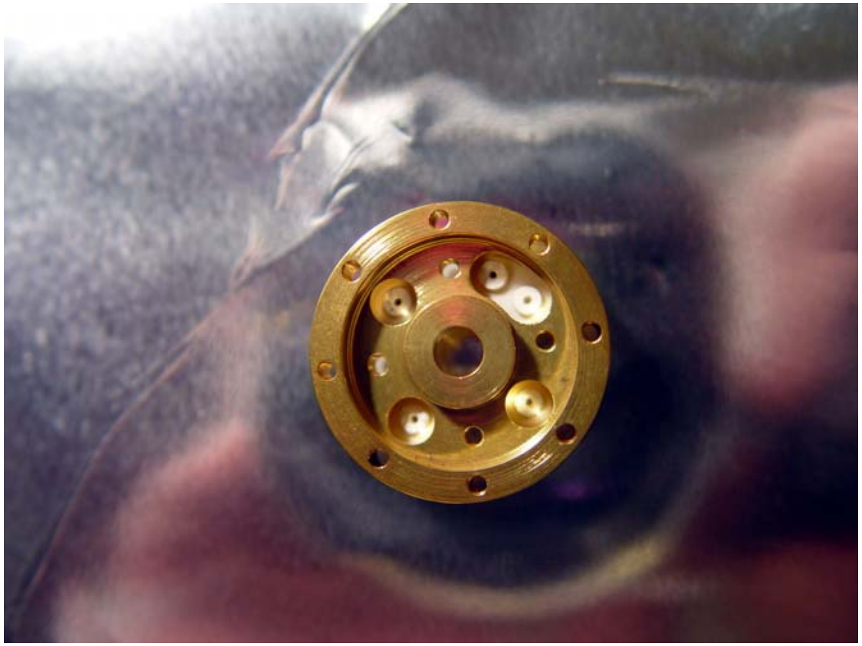
- Homebuilt STM in the Hersam lab at Northwestern University
- STM is a modified Lyding scanner

Scanner Construction: Piezotubes

Outer tube:
0.650" OD
0.570" ID
0.750" Long

Inner tube:
0.375" OD
0.315" ID
0.750" Long

Scanner Construction: Base Plug

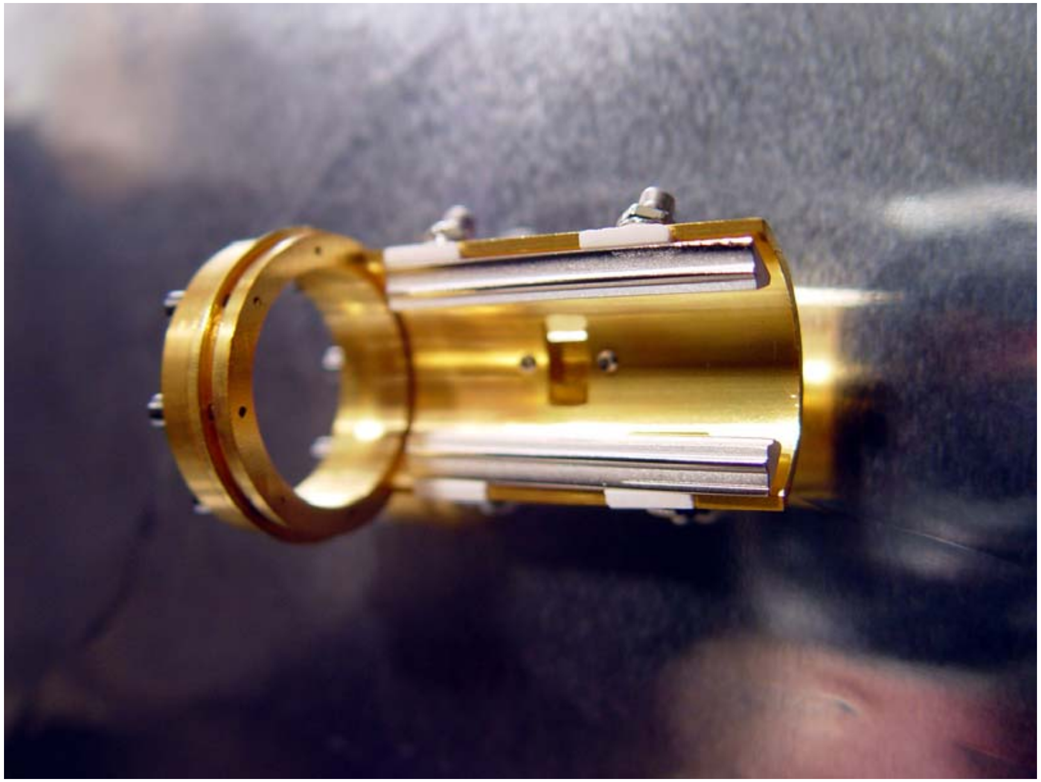


Front View

Rear View

Scanner Construction: Piezotubes Soldered into Base Plug

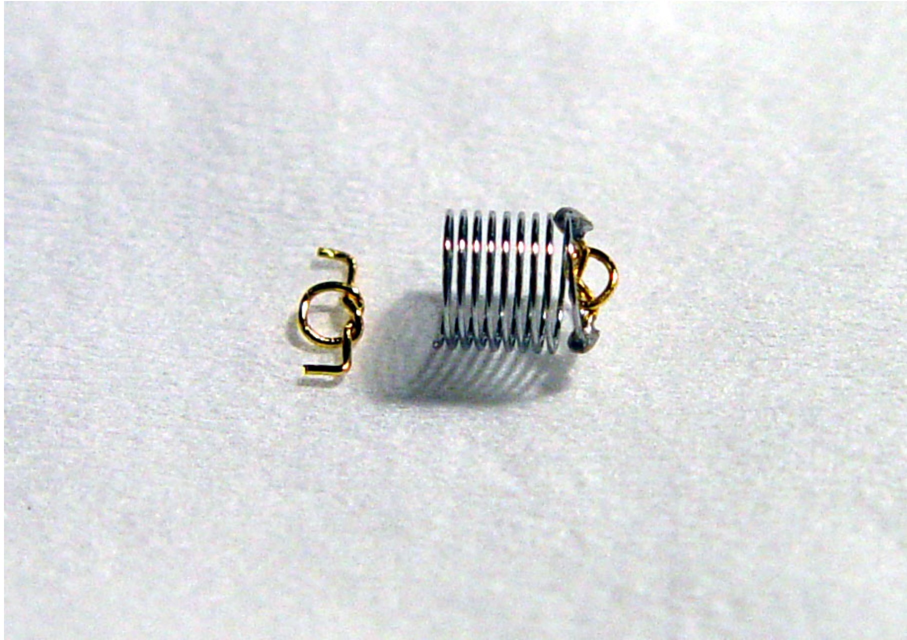
Scanner Construction:
Course Translation Platform

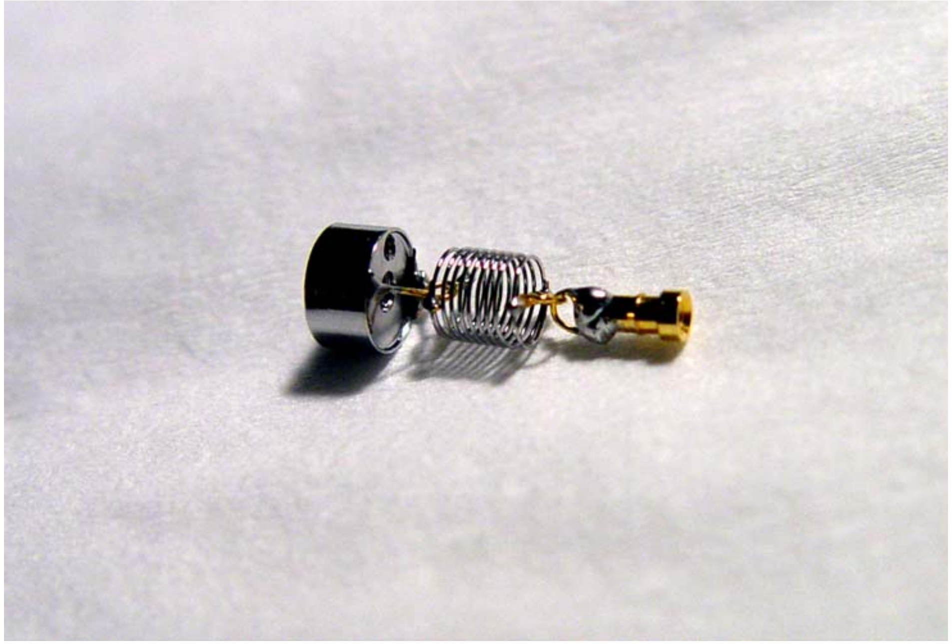


Scanner Construction: Course Translation Platform Soldered onto Outer Piezotube

Scanner Construction: End Cap Positioned onto Inner Piezotube

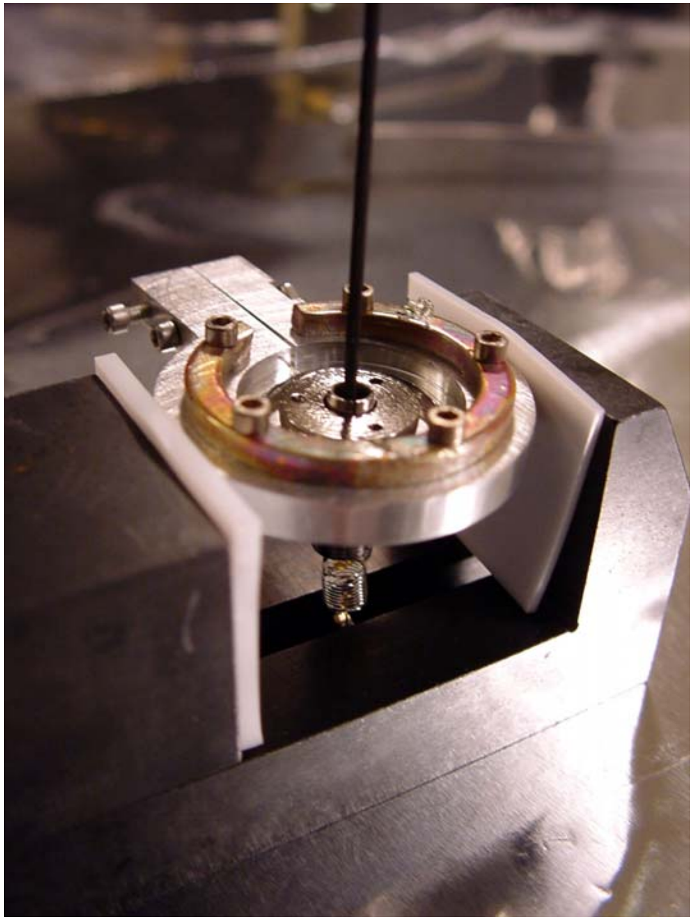
Scanner Construction: Tip Contact Assembly



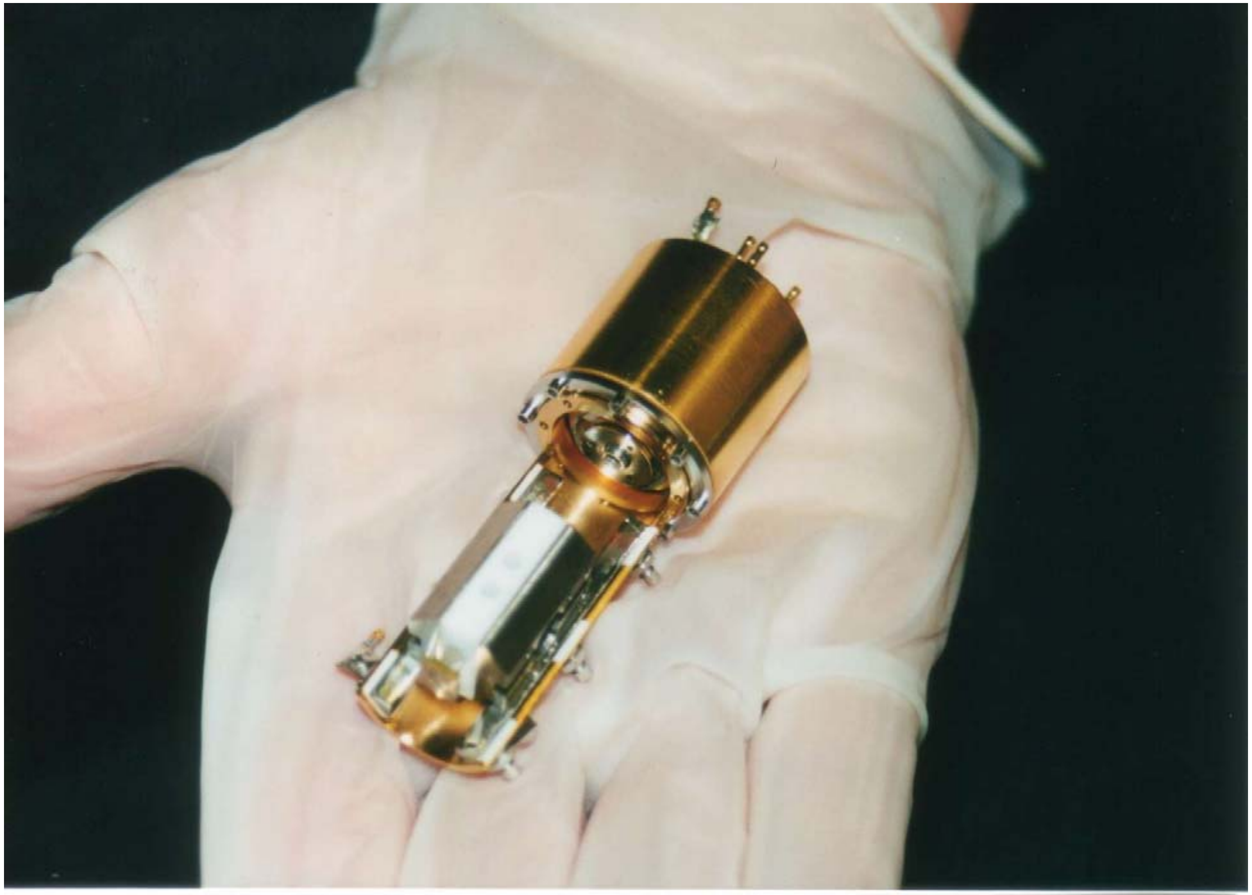


Scanner Construction: Full Tip Assembly

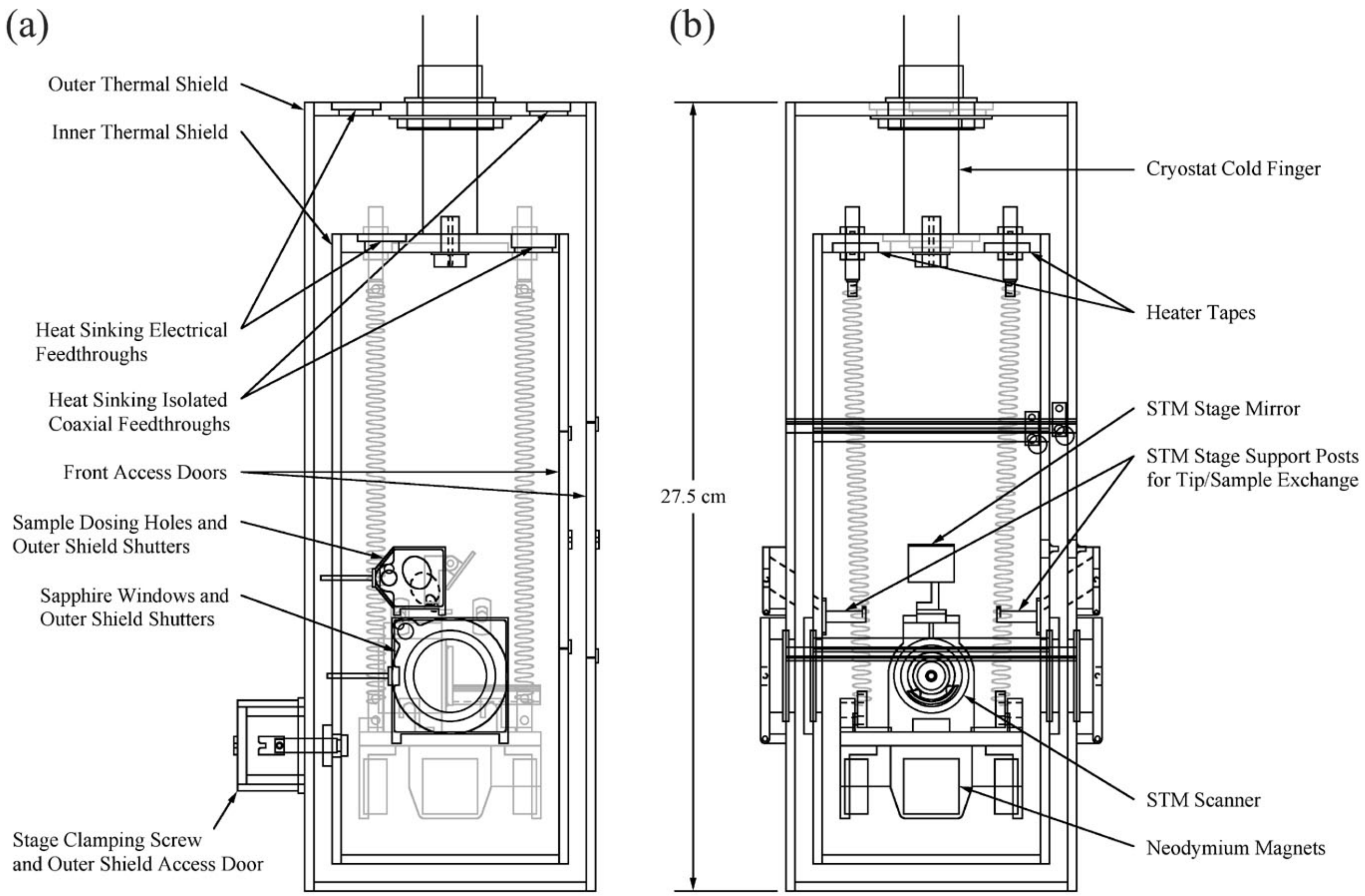
Scanner Construction: Adjusting Clamping Force on Sapphire Washer and Soldering into Inner Piezotube End Cap



Scanner Complete

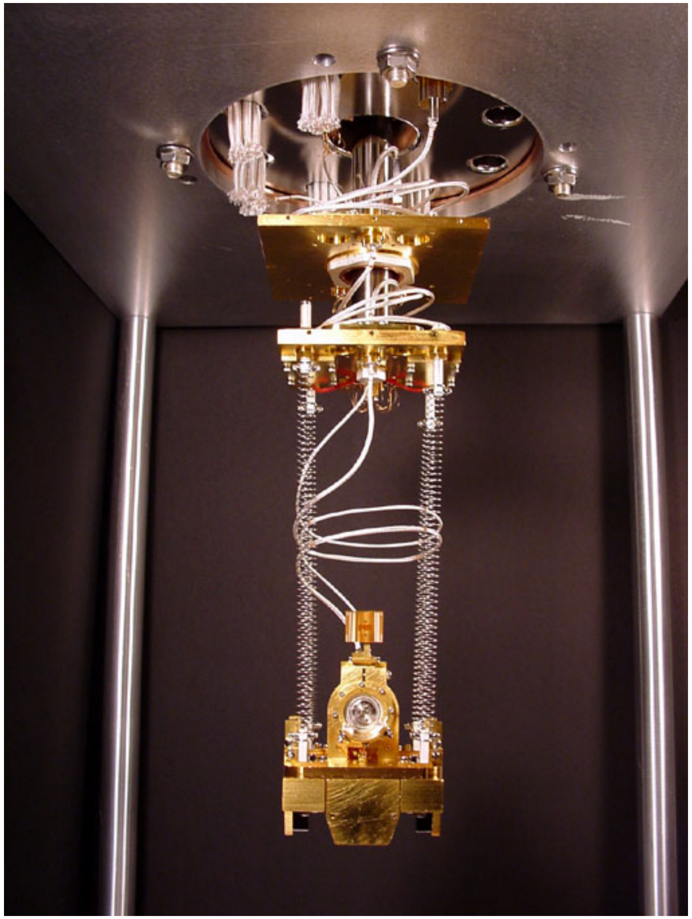


Cryogenic Variable Temperature UHV STM

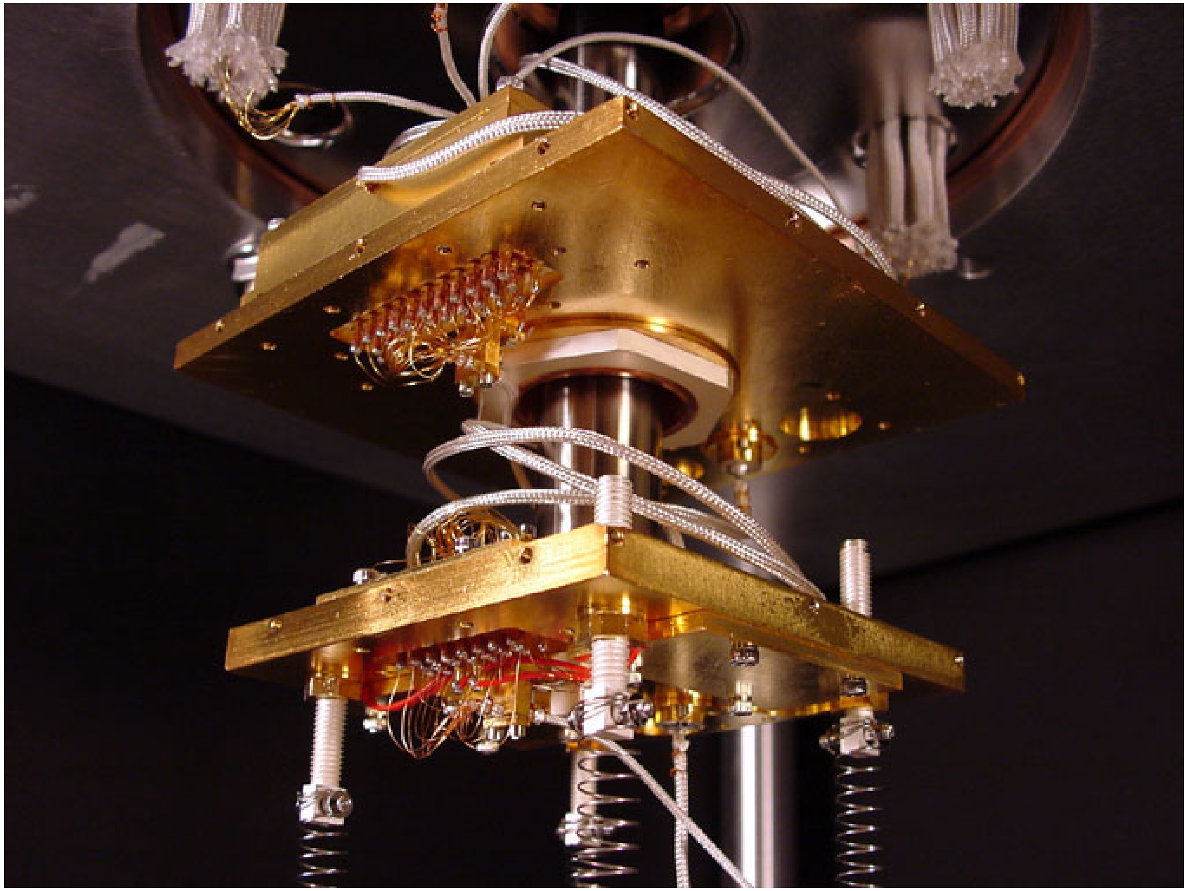


E. T. Foley, *et al.*, *Rev. Sci. Instrum.*, **75**, 5280 (2004).

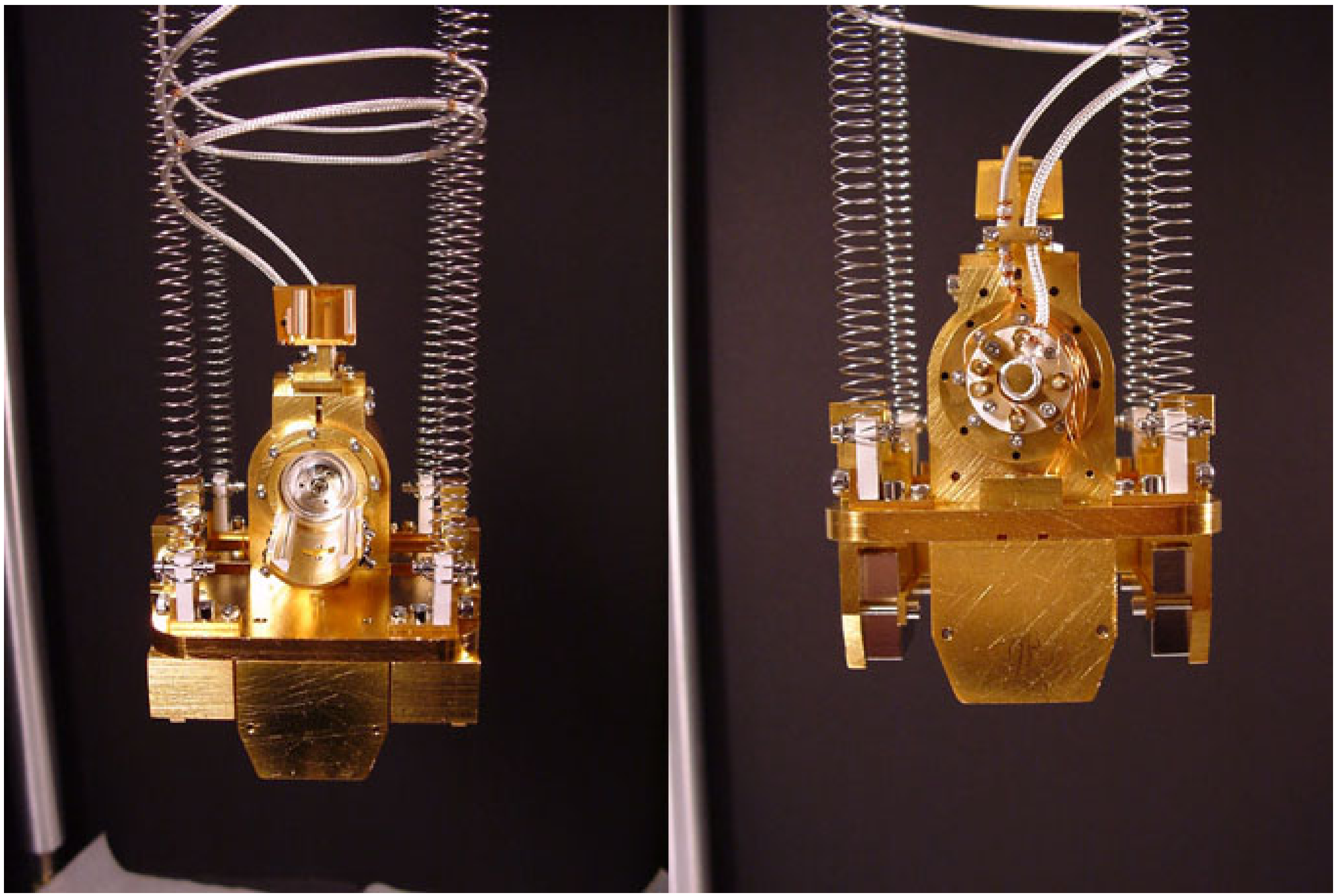
Vibration Isolation



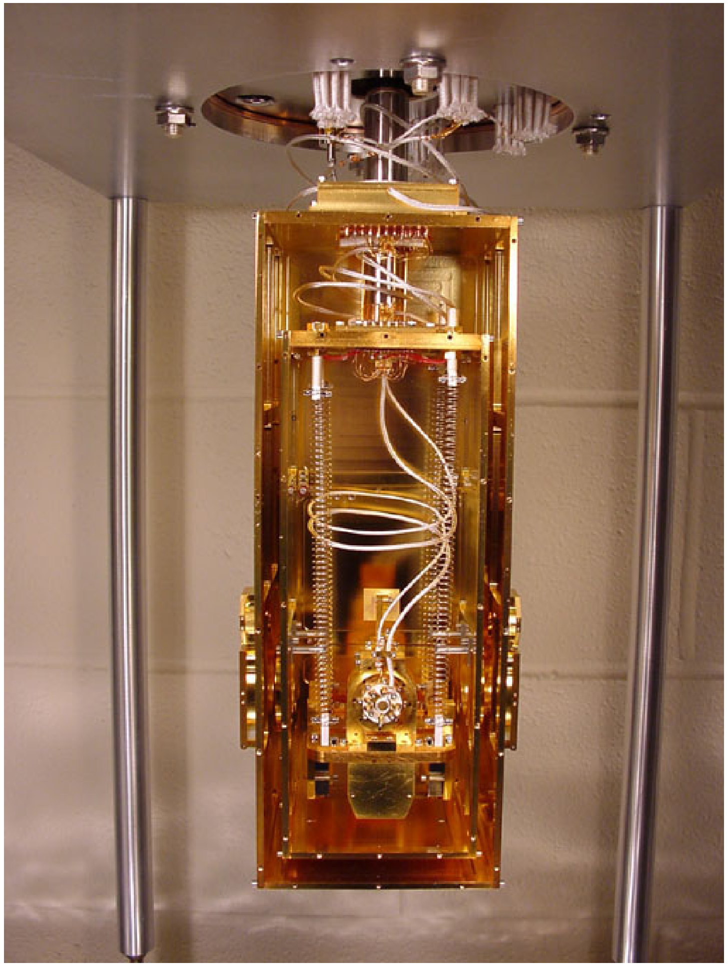
Detail of Roof Plate



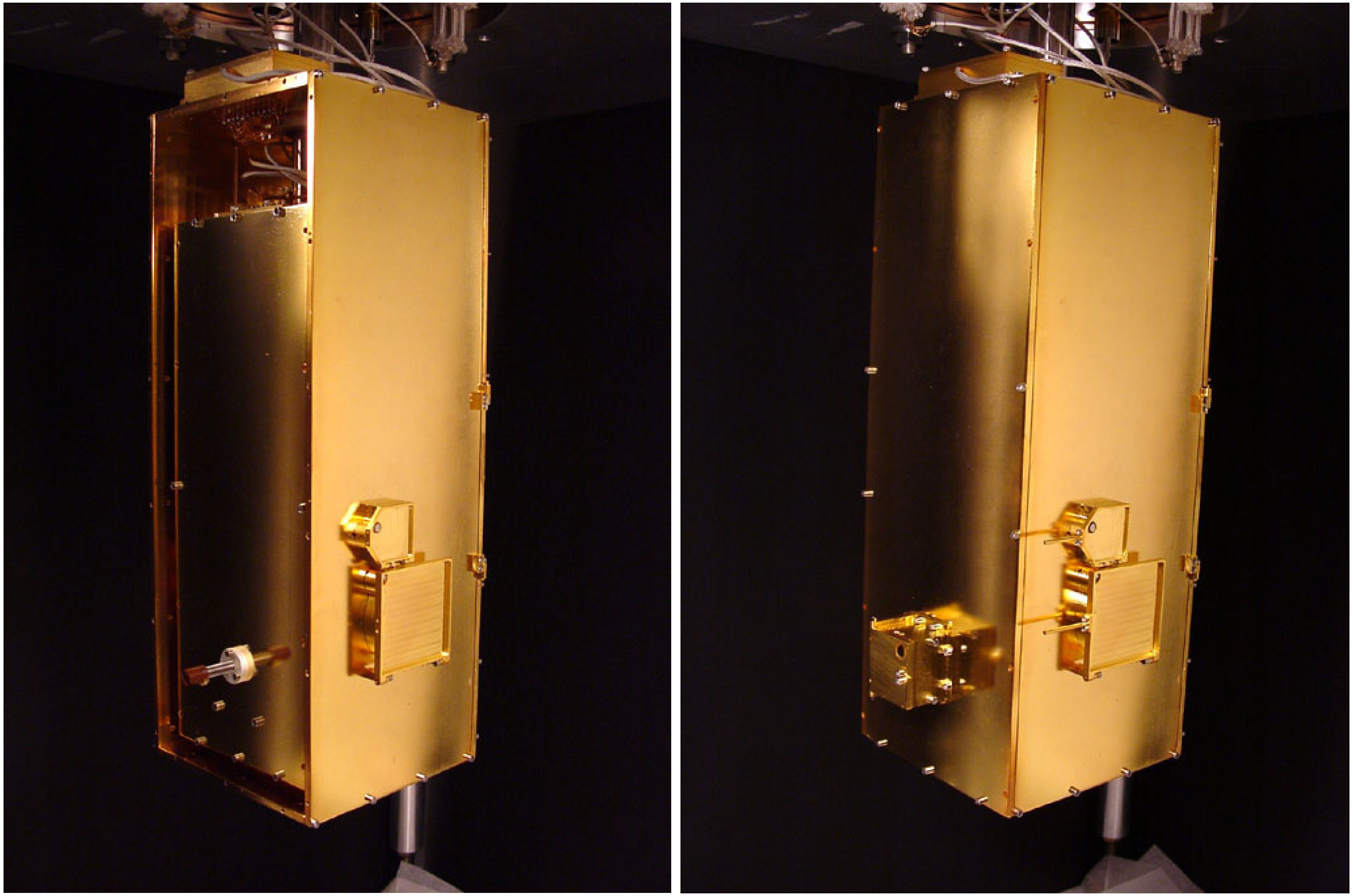
Detail of STM Stage



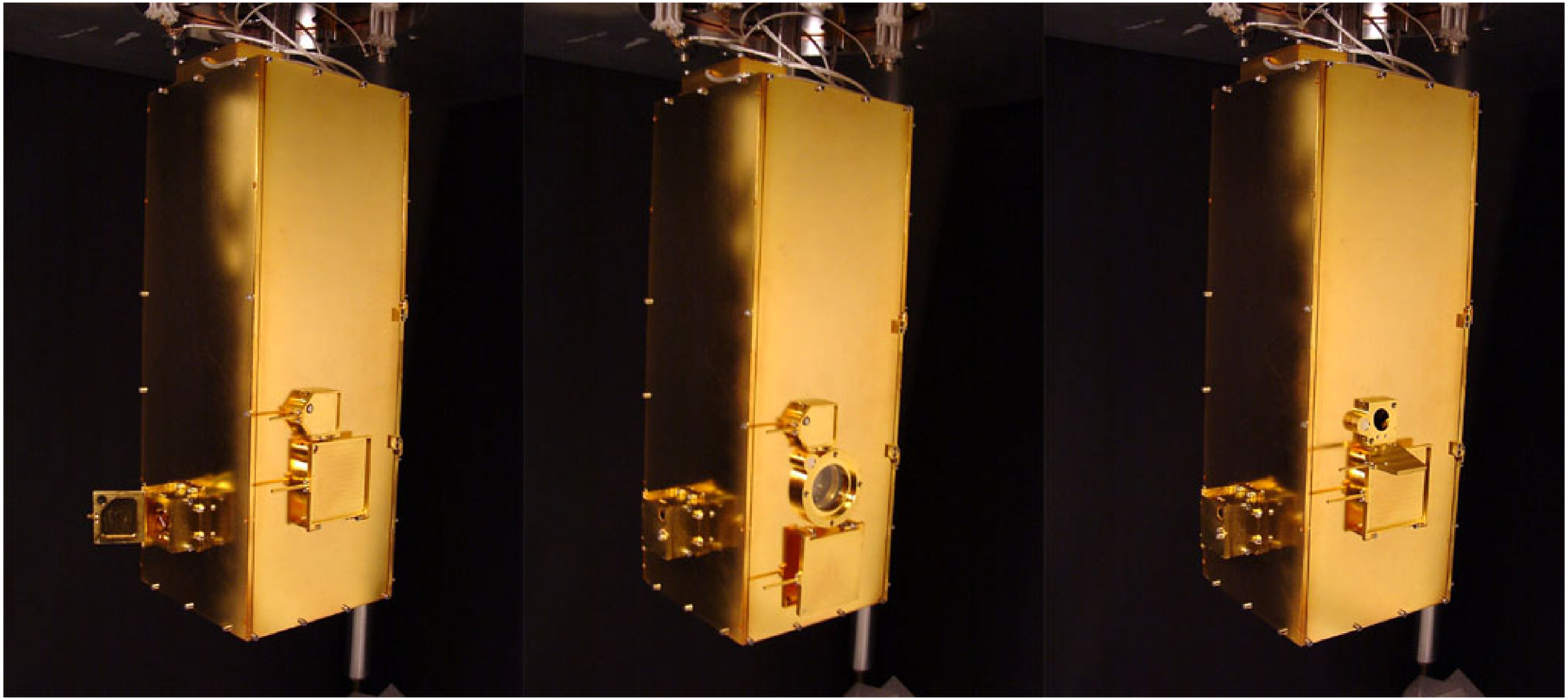
Thermal Shields with Back Panel Removed



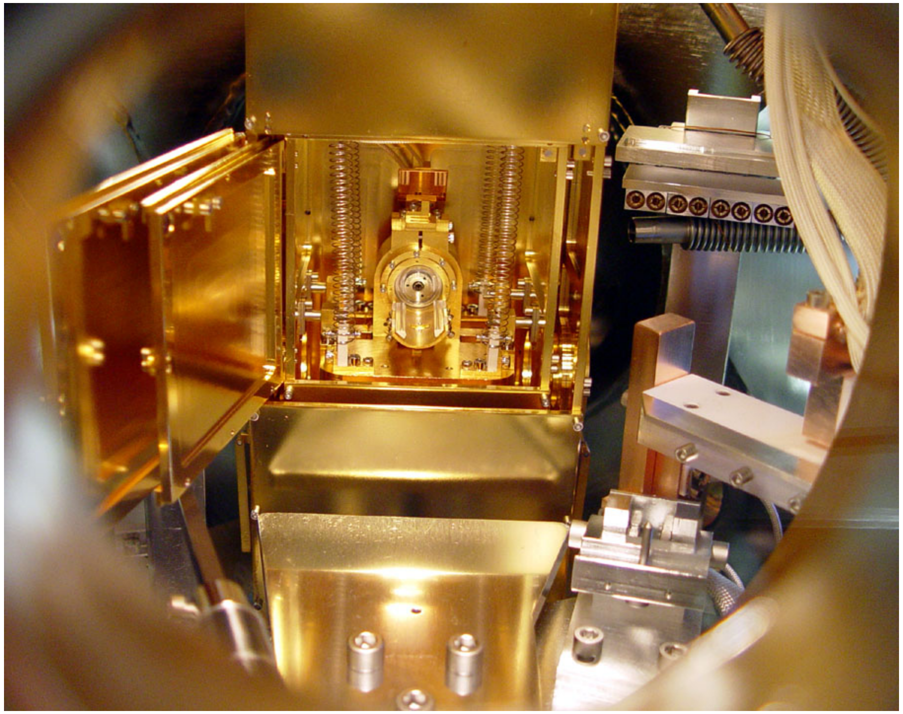
Stage Locking Screw for Cooldown



Rear Door and Shutter Action

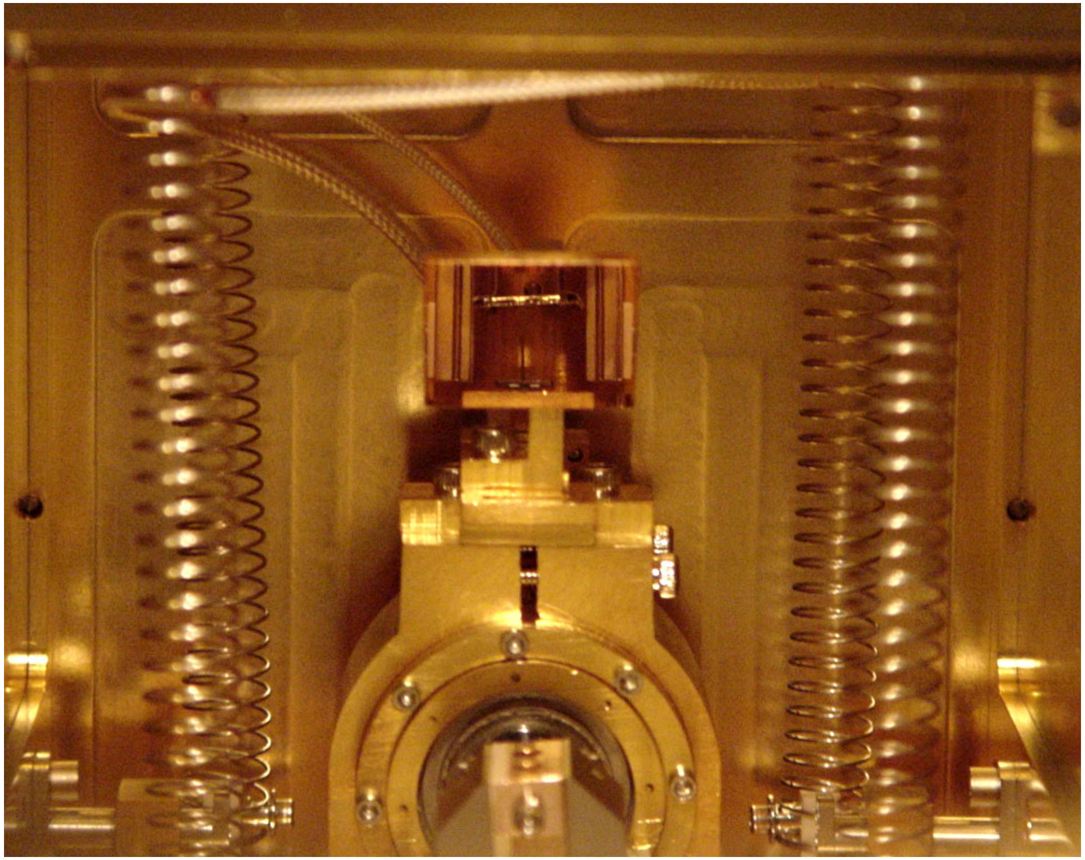


Front Doors Open for STM Access

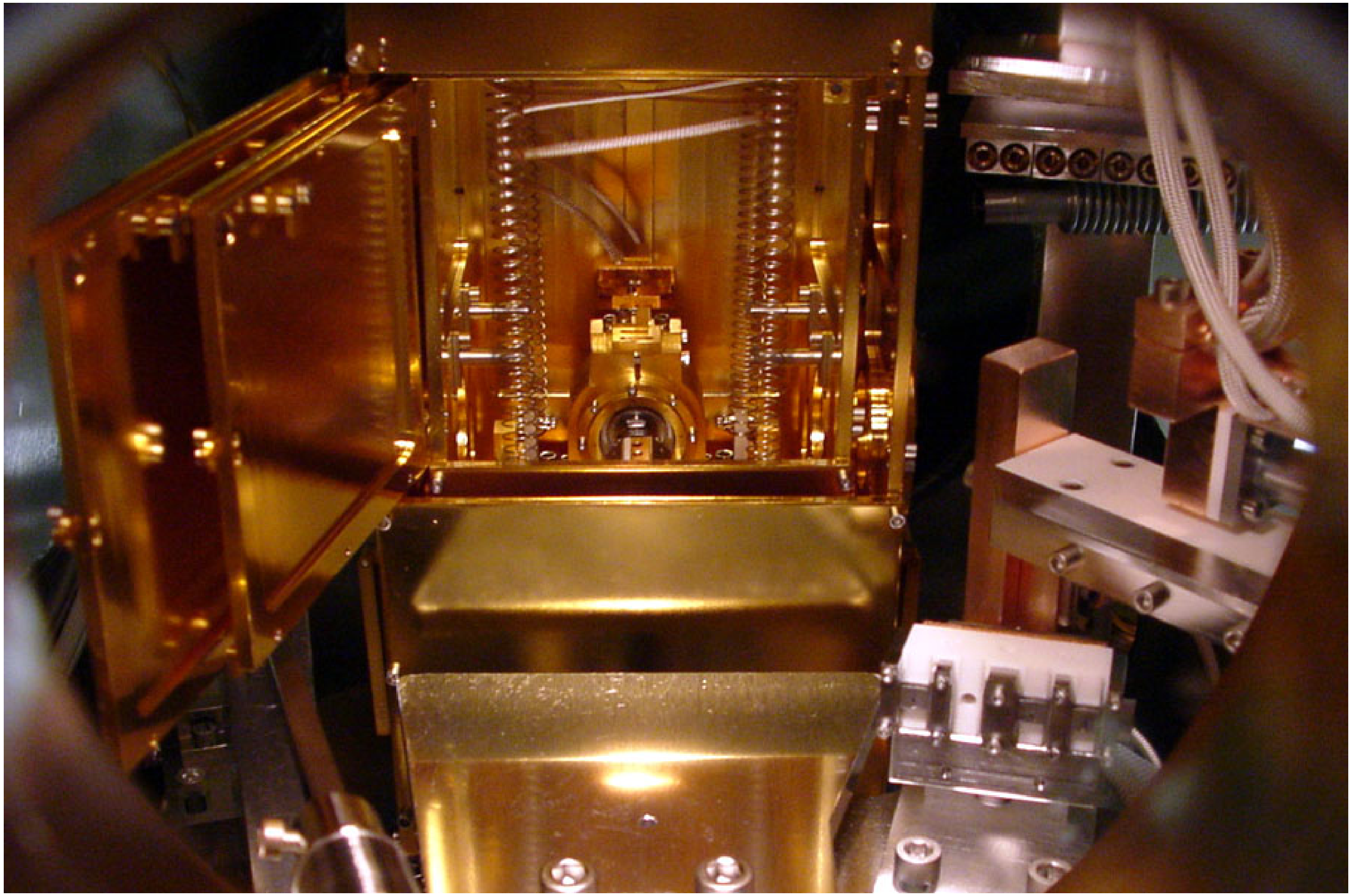


Sample and Probe Mounted for Scanning

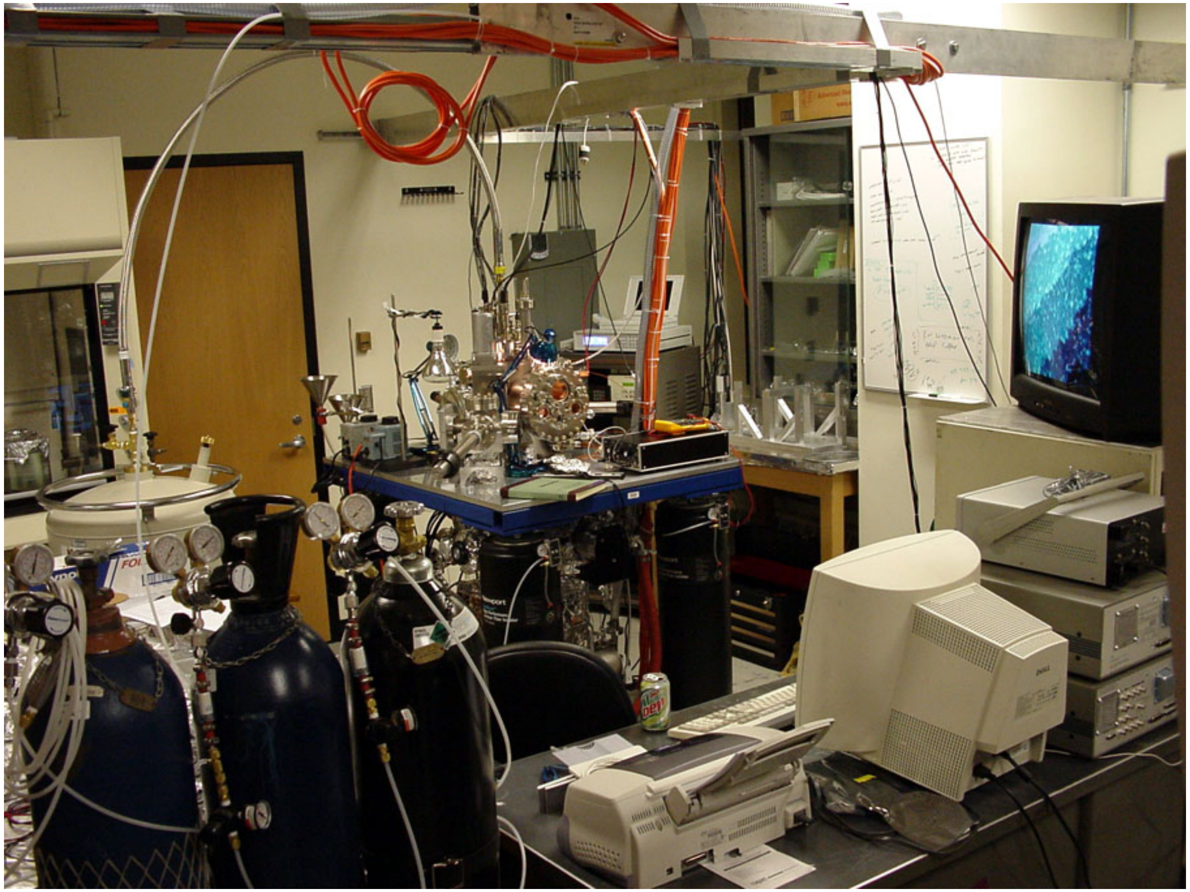
Mirror Allows for Top-Down View of Tip-Sample Junction



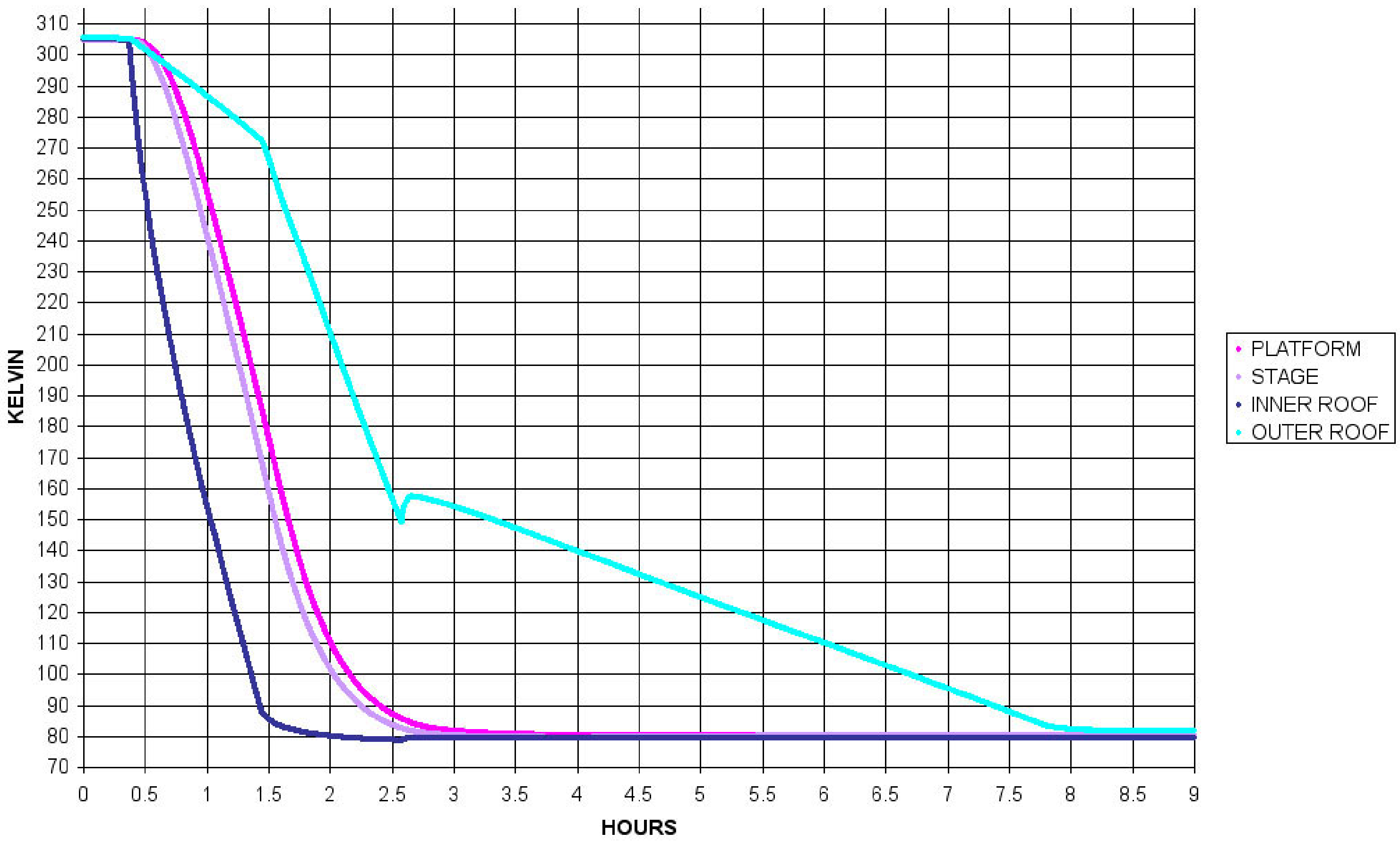
STM Suspended for Scanning



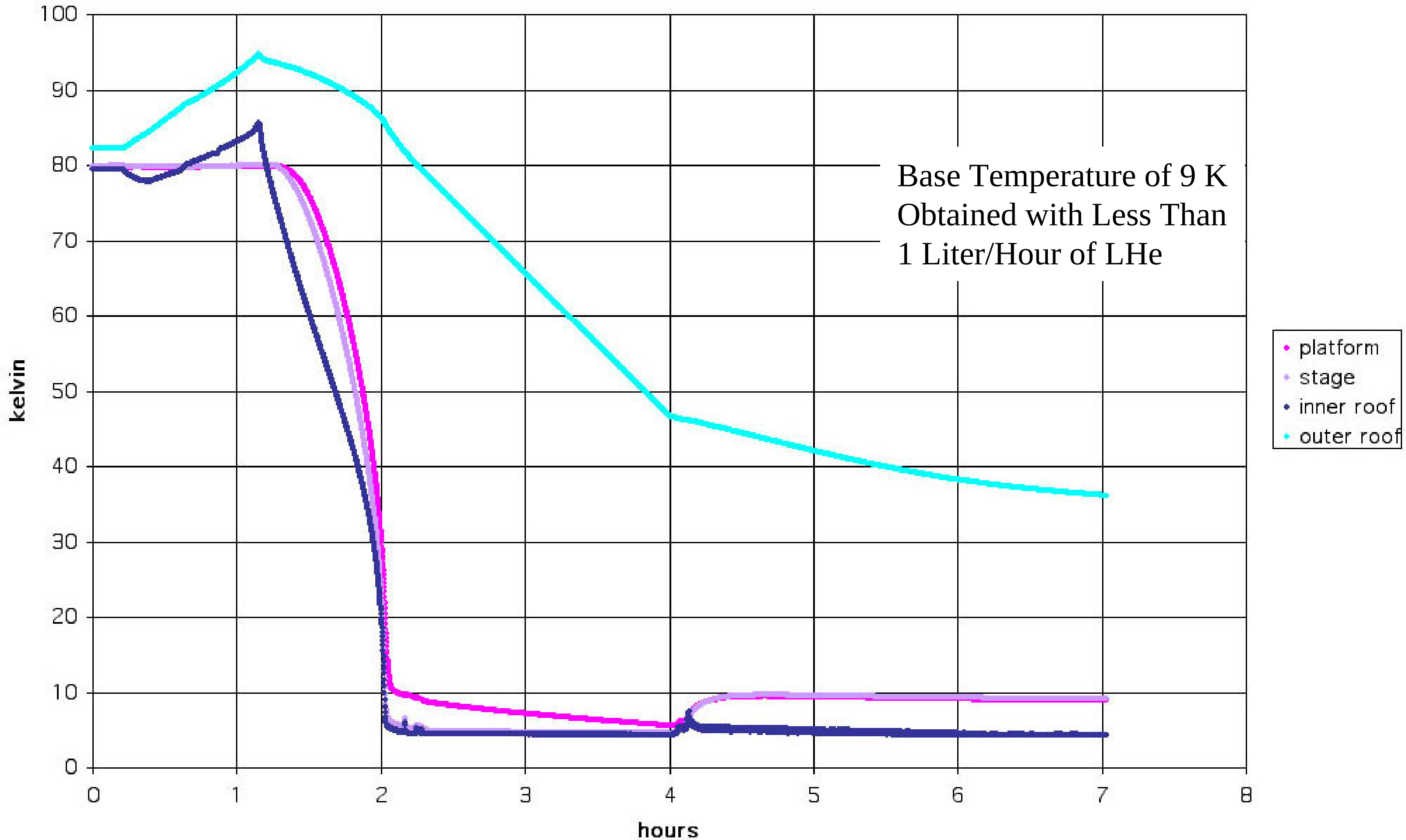
UHV Chamber and Liquid Helium Dewar



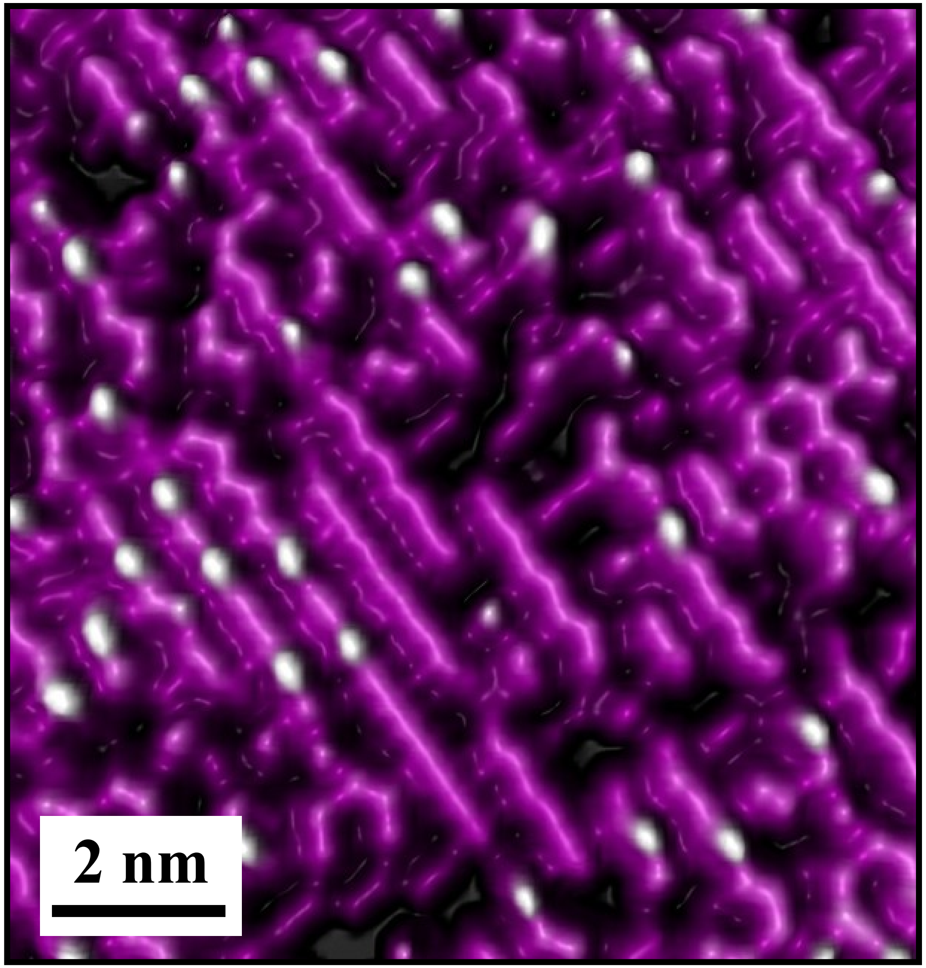
Cooling with Liquid Nitrogen



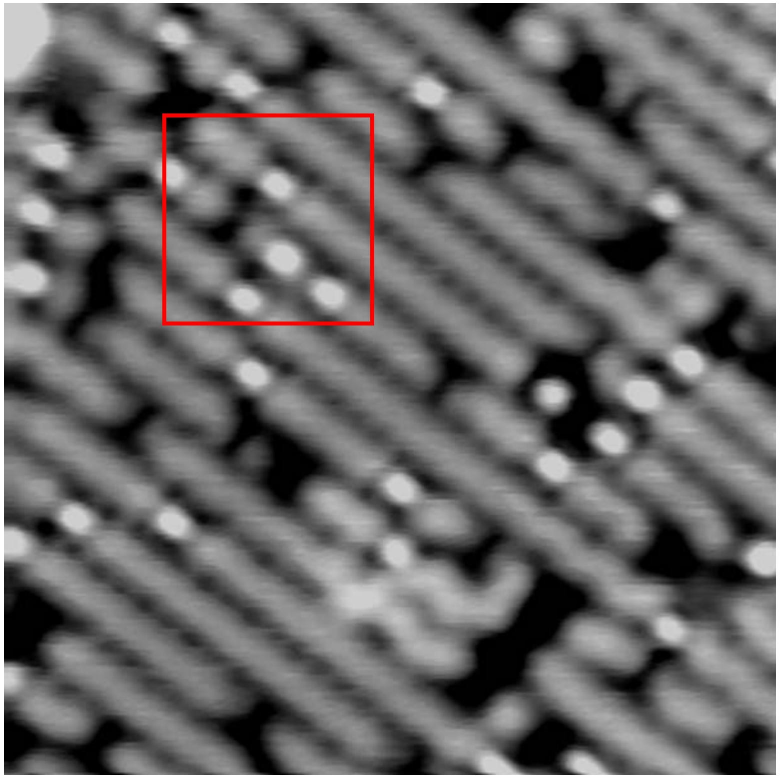
Cooling with Liquid Helium



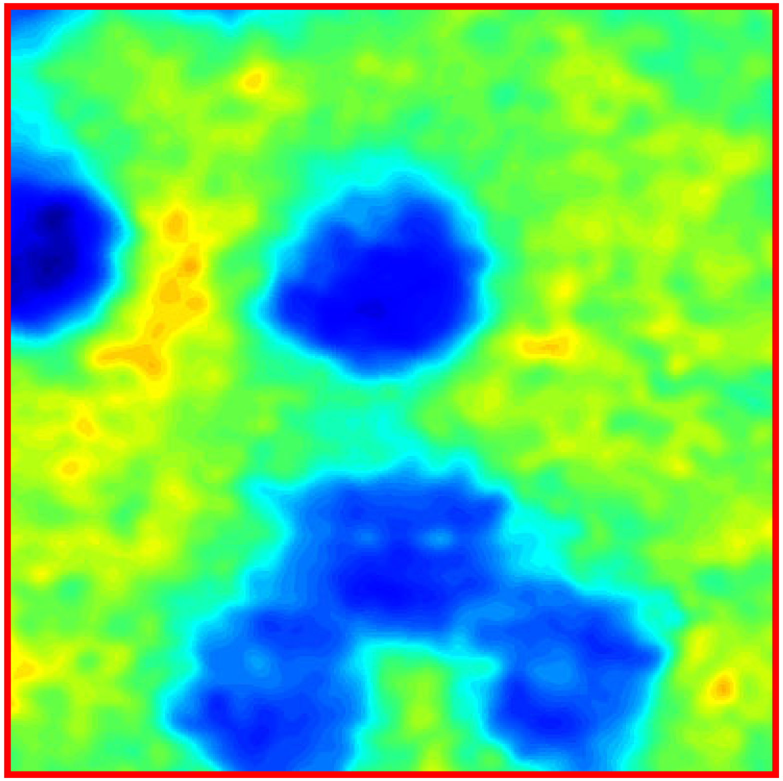
Si(100) Dosed with Cyclopentene at 80 K



dI/dV Imaging of Cyclopentene on Si(100) at 80 K

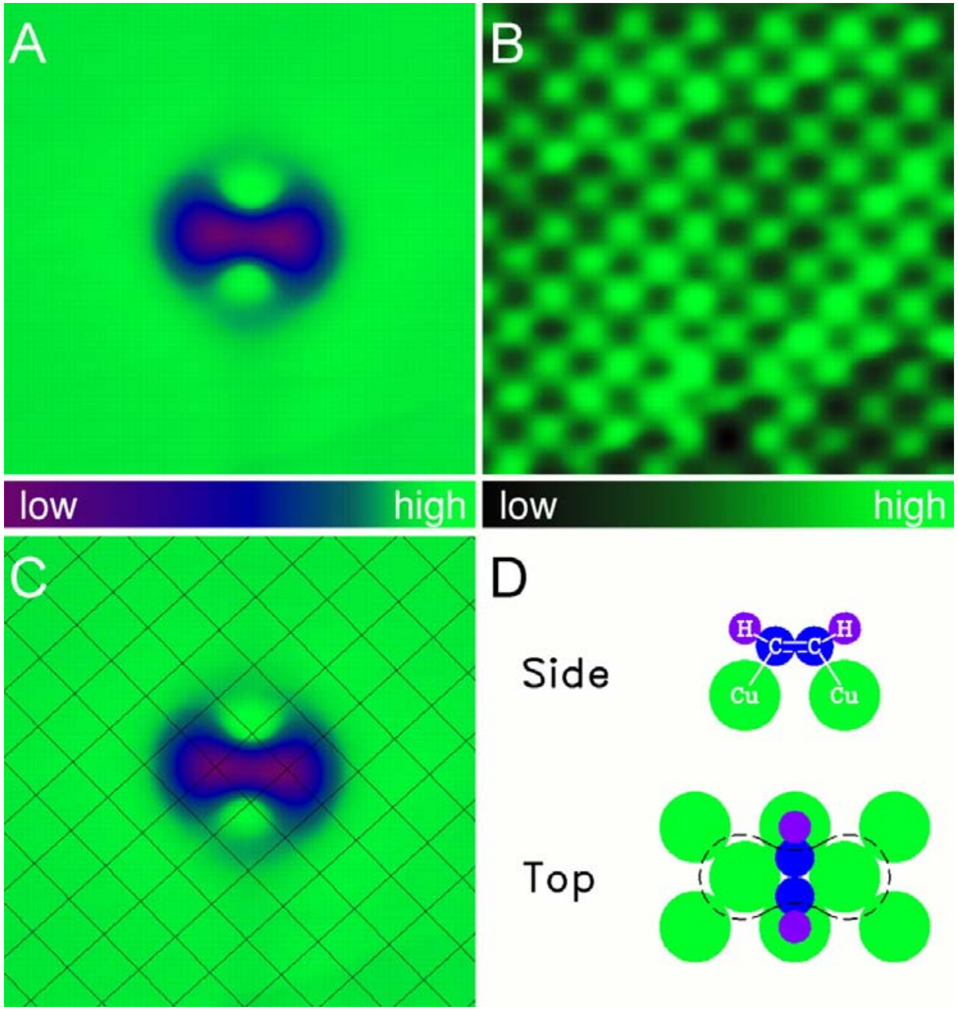


150 Å x 150 Å, -2.15 V, 0.1 nA



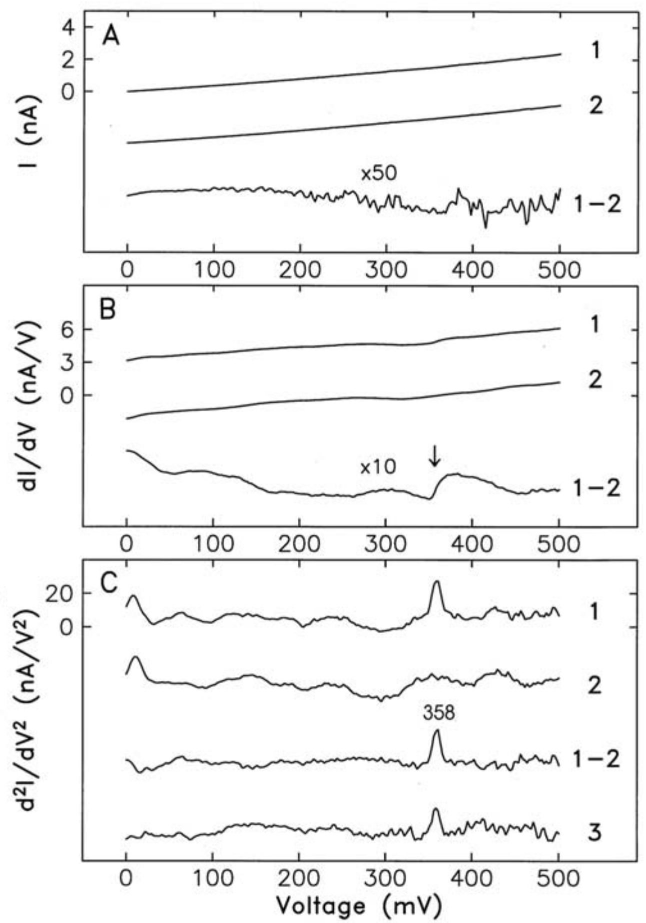
dI/dV Map at -2.8 V

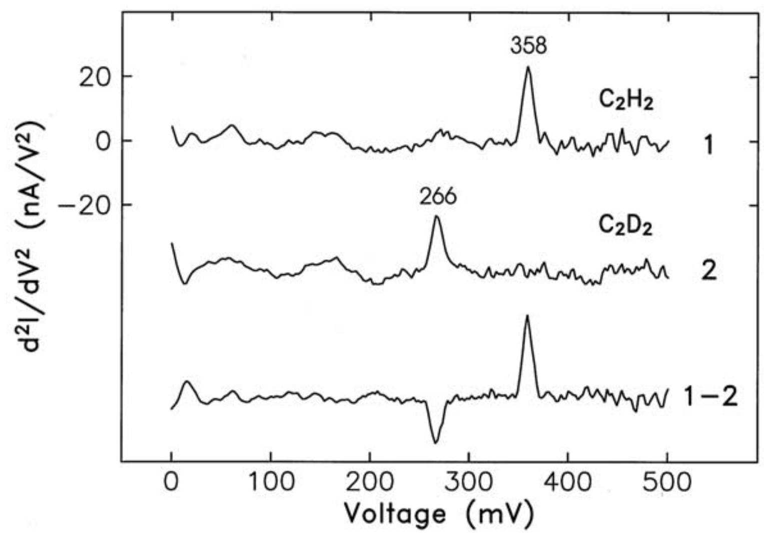
C_2H_2 on Cu(100)



B. C. Stipe, *et al.*, *Science*, **280**, 1732 (1998).

Inelastic Electron Tunneling Spectroscopy



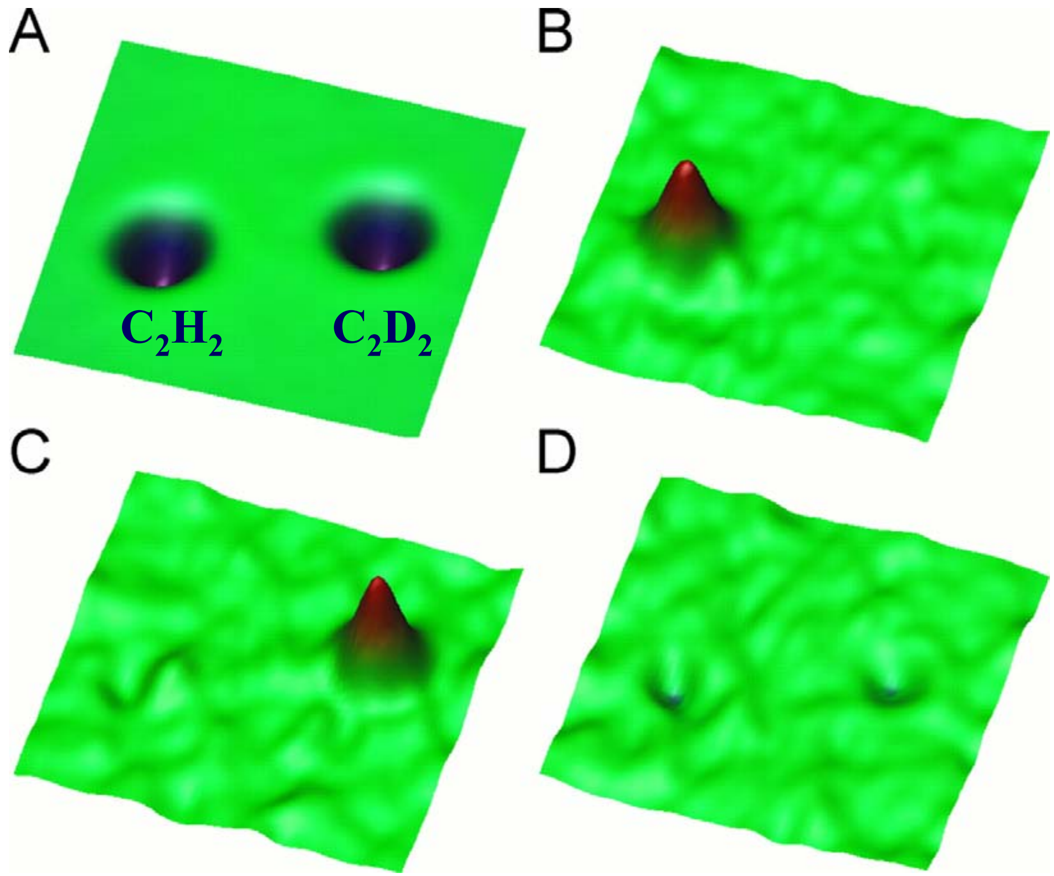


B. C. Stipe, *et al.*,
Science, **280**, 1732 (1998).

Spatial Maps of d^2I/dV^2

Topo

d^2I/dV^2 @ 358 mV



d^2I/dV^2 @ 266 mV

d^2I/dV^2 @ 311 mV

B. C. Stipe, *et al.*, *Science*, **280**, 1732 (1998).

Scanning Tunneling Microscopy Nanofabrication

Many nanofabrication schemes have been developed with STM (spatial resolution down to the single atom level):

(1) Initially demonstrated by Eigler in 1989
("IBM" written with atoms at cryogenic temperatures)

(2) Room temperature atom removal from Si(111) by Avouris

(3) Field evaporation of gold

(4) Electron stimulated desorption of hydrogen from Si(100)

Tunable Bond Formation with STM

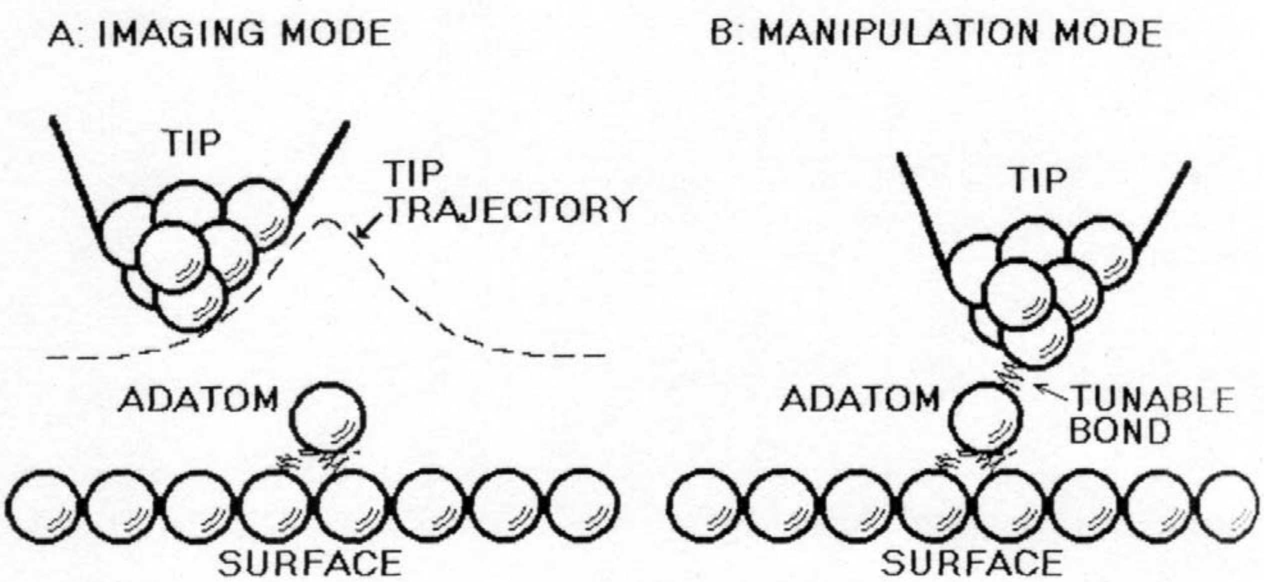


FIGURE 2. (A) In the imaging mode the tip is stabilized far enough above the surface so that the interaction between the tip and the adatom is negligible. (B) In the manipulation mode the tip is brought close enough to the adatom to drag the adatom along the surface. The force exerted on the adatom by the tip is due to the partially formed chemical bond between the tip and the adatom.

G. Timp, *Nanotechnology*, Chapter 11

Sliding Adatoms with STM

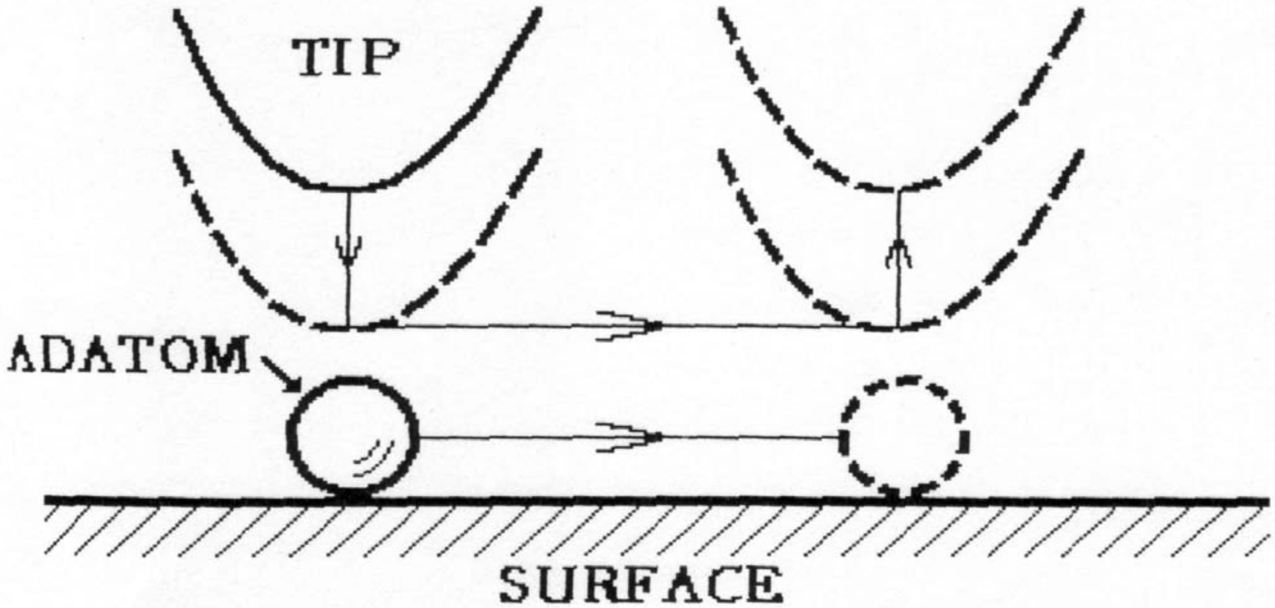
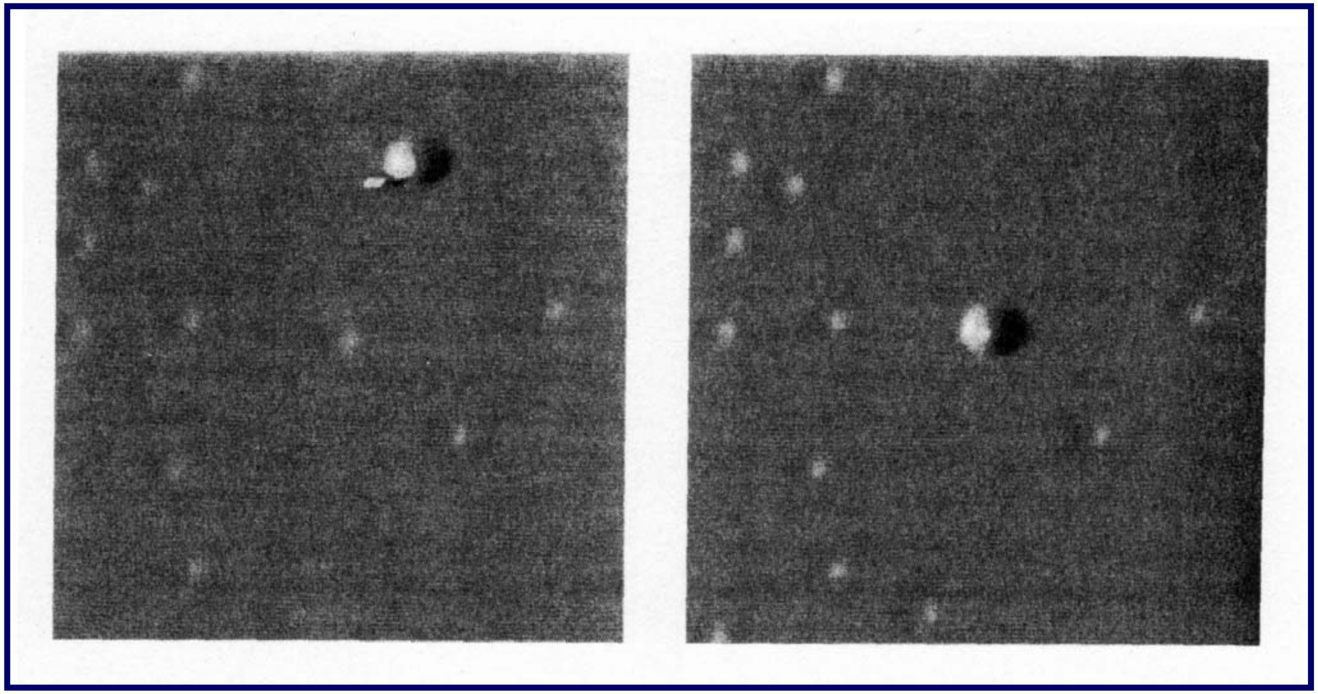


FIGURE 3. Schematic of the sliding process. The tip is placed above the adatom and then lowered to an empirically determined height at which the attractive interaction between the tip and the adatom is sufficient to pull the adatom along the surface. Once the adatom is moved to its final location, the tip is raised back to the height used for imaging, effectively terminating the tip-adatom interaction.

G. Timp, *Nanotechnology*, Chapter 11

The First Atom Moved with STM



Xenon on platinum → requires a defect to prevent tip-induced motion under normal scanning conditions

G. Timp, *Nanotechnology*, Chapter 11

STM Manipulation of Xenon on Nickel

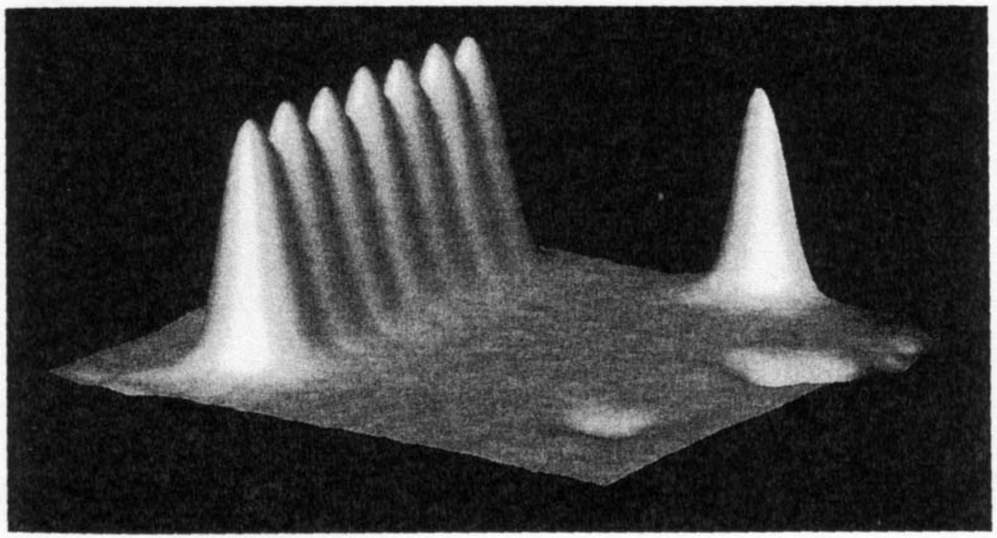


FIGURE 5. A row of seven xenon atoms constructed with the STM. The xenon atoms are spaced apart every other atom of the underlying nickel surface. The xenon atom cannot be packed together any tighter and remain in a single row. From building structures like this we learn about the strength of the xenon-xenon interaction relative to the strength of the in-plane interaction between the xenon atoms and the underlying nickel atoms.

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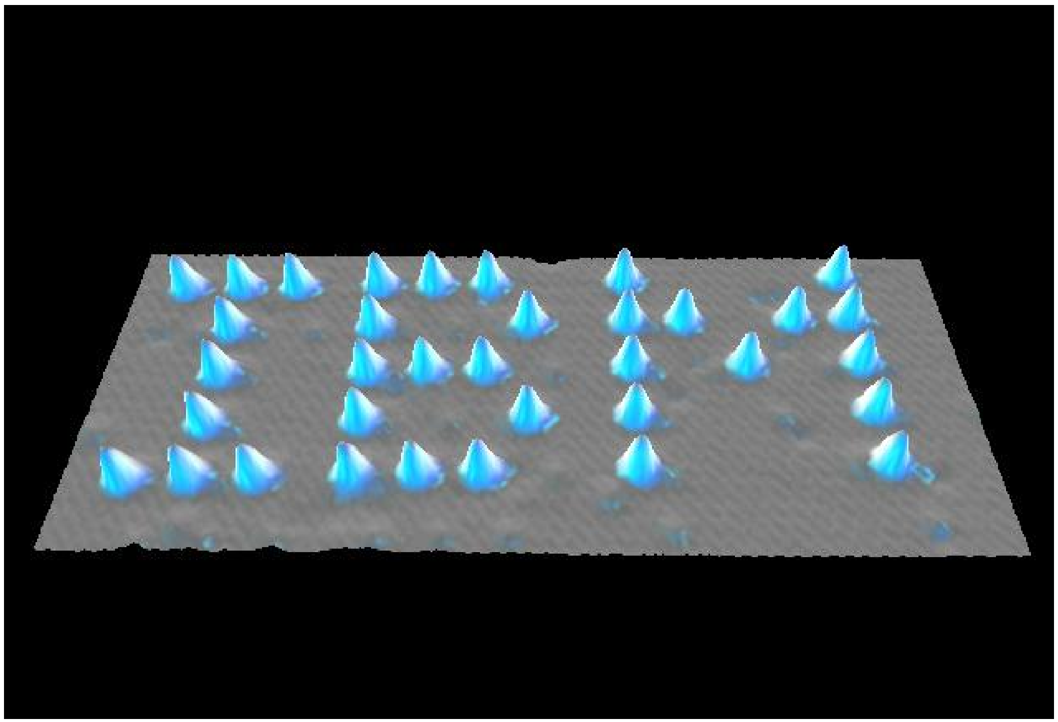
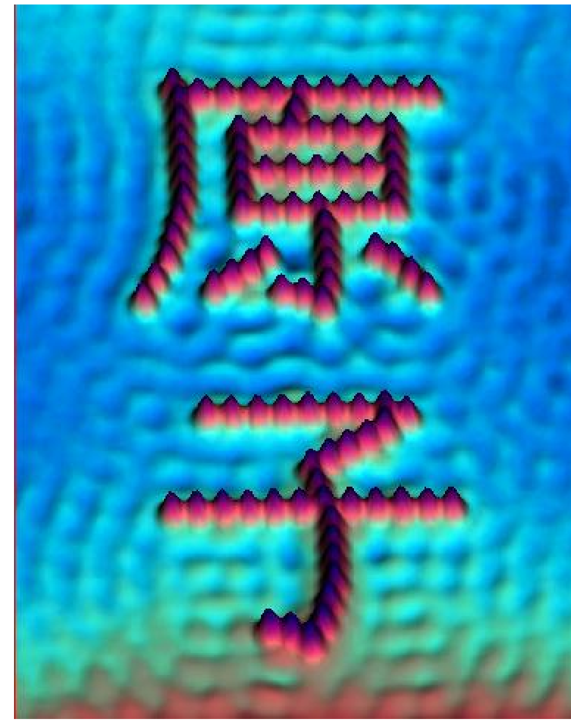
Nanograffiti

Kanji for atom:



Xenon atoms on Nickel (110)



Fe atoms on Cu(111)

Don Eigler, IBM Alamden, http://www.almaden.ibm.com/vis/stm/atomo.html